Synthetic Methods

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Boryl (Hetero)aryne Precursors as Versatile Arylation Reagents: Synthesis through C–H Activation and Orthogonal Reactivity

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Abstract: *(Pinacolato)boryl ortho-silyl(hetero)aryl triflates are presented as a new class of building blocks for arylation. They demonstrate unique versatility by delivering boronate or (hetero)aryne reactivity chemoselectively in a broad range of transformations. This approach enables the unprecedented postfunctionalization of fluoride-activated (hetero)aryne precursors, for example, as substrates in transition-metal catalysis, and offers valuable new possibilities for aryl boronate postfunctionalization without the use of specialized protecting groups.*

The development of versatile (hetero)arylation strategies is a key pursuit in organic synthetic methodology.[1] Dramatic advances on this front are exemplified by the use of aryl boronate reagents[2] and aryne intermediates.[3] Both participate in a seemingly inordinate range of reactions, including C–C, C–N, carbon–chalcogen and carbon–halogen bond formation. Aryl boronates have also attracted attention as organocatalysts,[4] as well as for medicinal[5] and materials[6] applications. Meanwhile, (hetero)arynes enable simultaneous, regioselective functionalization at two adjacent carbon atoms[7] and may be generated under mild conditions from *ortho*-silyl (hetero)aryl triflates using fluoride.[8] Such advantages have fueled their increasing popularity in the synthesis of natural products,[9] functional materials,[10] and organometallic compounds.[11]

The versatility of aryl boronates and *ortho*-silyl aryl triflates renders the prospect of their selective postfunctionalization exceptionally attractive. It promises greatly to broaden the range of possible derivatives, obviate tedious/inefficient de novo syntheses, and enable iterative approaches to their elaboration.[12] However, the same mild and versatile reactivity that imparts aryl boronates and *ortho*-silyl aryl triflates with such broad appeal makes their postfunctionalization commensurately more challenging.

For aryl boronates, responses to this problem have largely relied on the use of protecting groups to mitigate the reactivity of the boron center with respect to that of (pseudo)halide,[13] stannane,[14] or orthogonally protected boronate[15] groups present on the same arene. However, this approach has been exploited almost exclusively in C–C bond coupling; methods to introduce other valuable functionality remain scarce.[16]

Remarkably, the postfunctionalization of *ortho*-silyl aryl triflates has never been reported, despite their growing popularity and the passing of three decades since the seminal report by Kobayashi and co-workers on their use as aryne precursors.[8] Variants requiring even ostensibly simple substitution patterns often need inconvenient, multistep preparation.

We envisaged that the unique reactivities of aryl boronates and arynes could be harnessed for their mutual, chemoselective postfunctionalization (Figure 1). This approach would address both problems from common intermediates and offer versatile building blocks for arylation. Elegant recent studies by Akai and co-workers on the unusual influence of 3-boryl substituents over the regioselectivity of benzyne capture stands as the only previous juxtaposition of aryne and boronate reactivities.[17] However, the requirement that the boronate be placed at the benzyne C3 position in these studies necessitated multistep preparation and revealed an incompatibility with fluoride in the absence of extremely robust protecting groups.[17c] It also seemingly precluded use of the boronate prior to capture of the aryne and therefore the prospect of postfunctionalizing the aryne precursor. We reasoned that the remarkable functional-group tolerance of iridium-catalyzed C–H borylation[18] and its preference for the least sterically hindered position of simple arenes[19] would

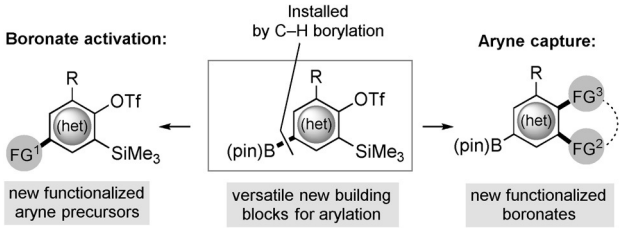

Figure 1. Underlying concept of this study. B(pin) = (pinacolato)boryl, Tf = trifluoromethanesulfonyl.

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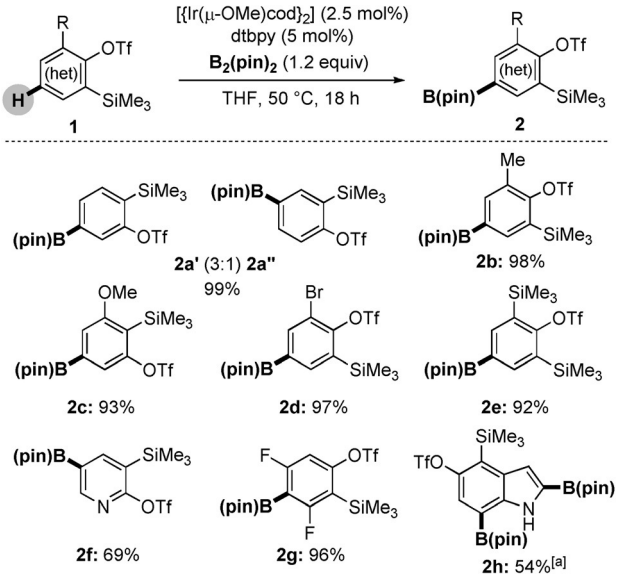
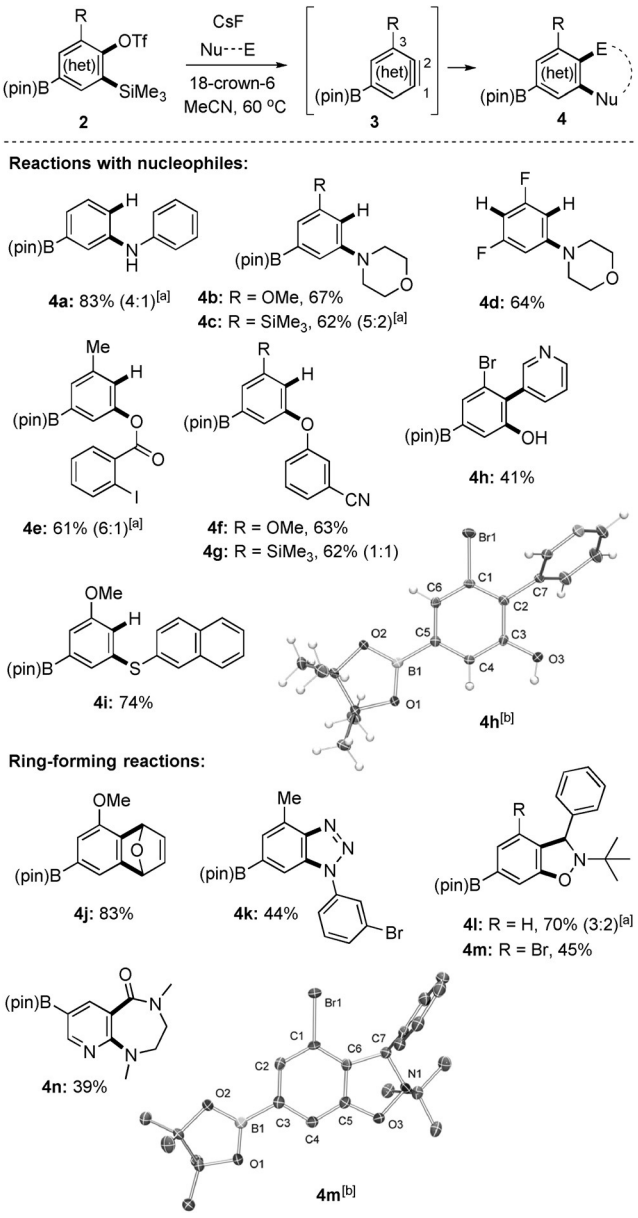


Scheme 1. Iridium-catalyzed C–H borylation of aryne precursors **1**. [a] The reaction was carried out using 2 equivalents of $B_2(pin)_2$ in a reaction time of 42 h. cod = 1,5-cyclooctadiene.

provide a direct way to introduce a B(pin) substituent selectively into precursors **1**, thereby preserving various R groups at C3, where they are known to influence aryne reactivity most profoundly.[20]

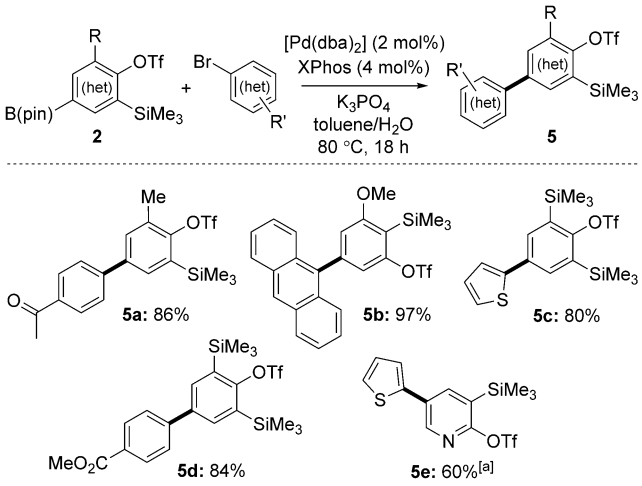
At the outset of our study, we found that the treatment of benzyne precursor **1a** (R = H) with [{Ir(μ-OMe)cod}$_2$], 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbpy), and $B_2(pin)_2$ under the conditions shown in Scheme 1 gave **2a** quantitatively as a 3:1 mixture of regioisomers. The scope of the reaction was extended to the synthesis of **2b–g** with complete regioselectivity and generally excellent yields on scales up to 2 g. The reaction of 4,5-indolyne precursor **1h**[21] under the same conditions gave inseparable mixtures of C2- and C7-borylated products; the use of more $B_2(pin)_2$ led exclusively to diboronate **2h**.[22]

We next explored chemoselective aryne generation from **2**. We found that CsF (4 equiv) and 18-crown-6 (1 equiv) in MeCN enabled a broad range of functionalization reactions (Scheme 2), including attack by N- (products **4a–c**), O- (products **4e–g**), and S-based nucleophiles (product **4i**), as well as [4+2] cycloaddition (product **4j**), cyclization with an aryl azide[23] (product **4k**) or nitrone (product **4l**,**m**), and insertion into a cyclic urea[24] (product **4n**). An exception was substrate **2g**, which invariably succumbed to rapid deborylation (to give **4d**),[25] as is common for polyfluoroaryl boronates.[26] Substrate **3a** (R = H) underwent preferential attack by heteroatoms at the carbon atom *meta* to the B(pin) group (products **4a**,**l**). Benzynes are usually biased by electronegative substituents to favor attack by nucleophiles at the distal carbon atom of the triple bond;[27] we attribute the opposite selectivity in the formation of **4a** and **4l** to the electropositive character of boron.[17a–d] Otherwise, the regioselectivity of aryne capture was governed by the R group. For example, the OMe group of **2c** directed nucleophilic addition exclusively to C1 of the corresponding aryne **3c** (products **4b**,**f**,**i**), whereas **2e** gave mixtures of regioisomers (products **4c** and **4g**) arising from the competing steric and electronic influences of the $SiMe_3$ substituent.[28] The activation of **2d** in the presence of pyridine *N*-oxide gave exclusively the 3-substituted pyridine **4h** through a rearrangement.[29]

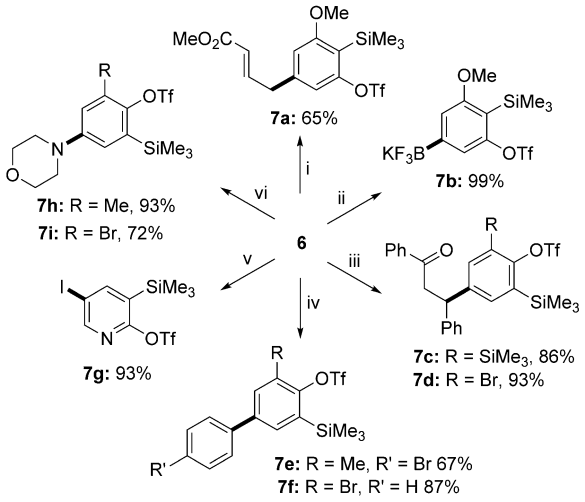


Scheme 2. Elaboration of boronates **2** through (hetero)aryne trapping. [a] A mixture of regioisomers was obtained; the major regioisomer is shown. [b] Crystal structure. Ellipsoids are drawn at 50% probability.

In most cases, the trapping reagent for boryl (hetero)arynes **3** was chosen to highlight the difficulty in accessing the anticipated products by established borylation methods in the final step. Thus, the halogen substituents in **4e**, **4h**, **4k**, and **4m** would make problematic their synthesis by borylation relying on lithiation or Pd catalysis.[15c,30] Similarly, the presence of several sterically accessible Ar–H bonds in **4e–i** and **4k–m** precludes their selective preparation by iridium-catalyzed C–H borylation.[19,31] The presented method is therefore a valuable and systematic new approach to aryl boronate postfunctionalization with a wide variety of func-



Scheme 3. Arylation of precursors **2** by SMC. [a] Reaction conditions in this case: $[Pd(dba)_2]$ (4 mol%), XPhos (8 mol%), K_2CO_3 (3 equiv), toluene/H_2O, 80 °C, 20 h. dba = dibenzylideneacetone, XPhos = 2-dicyclohexylphosphanyl-2′,4′,6′-triisopropylbiphenyl.

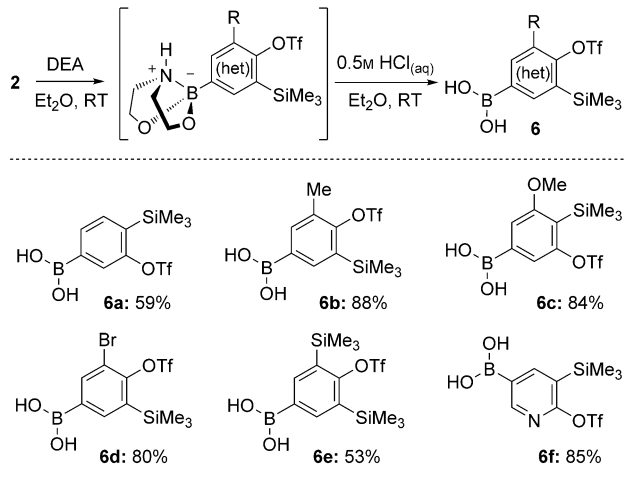


Scheme 5. Transformations of aryl boronic acids **6**: i) palladium-catalyzed allylation; ii) boronate conversion; iii) rhodium-catalyzed 1,4-conjugate addition; iv) palladium-catalyzed arylation with $[Ar_2I]X$; v) copper-catalyzed iodination; vi) Chan–Lam amination.

tional groups. Furthermore, no examples have been reported previously in which the convenience of fluoride-induced aryne generation was possible without concomitant loss of the boronate or the use of specialized protecting groups.

We next addressed the chemoselective manipulation of the boronate group of **2** to effect further *ortho*-silyl (hetero)aryl triflate postfunctionalization. Suzuki–Miyaura coupling (SMC) proceeded very well with various (hetero)aryl bromides without compromising the *ortho*-silyl triflate moiety (Scheme 3). We anticipate that this method will provide a flexible route to novel substituted polyaromatic systems, for which arynes are increasingly exploited as building blocks.[10] Competitive activation of the bromide and/or *ortho*-silyl triflate unit of **2d** was circumvented by a complementary strategy with diaryl iodonium reagents (see below).

To extend the utility of the boryl group for aryne-precursor postfunctionalization, compounds **2** were deprotected by treatment with diethanolamine (DEA) and acid hydrolysis.[32] This mild, expedient method furnished boronic acids **6** (Scheme 4), which proved indefinitely stable at room temperature in air.[25]



Scheme 4. Deprotection of **2** to give the parent boronic acids. In each case the corresponding boroxine was formed as a minor by-product; yields are given with respect to boron.

Boronic acids **6** participated in a broad selection of high-yielding transformations with complete preservation of the *ortho*-silyl triflate (Scheme 5). The conversion of **6c** through palladium-catalyzed allylation into **7a** or trifluoroborate[33] **7b** is notable for its use of KF (up to 4 equiv), which is also commonly exploited to activate *ortho*-silyl aryl triflates. It demonstrates the following practicable order of functional-group reactivity with respect to fluoride: $B(OH)_2$ > *ortho*-silyl triflate > B(pin), and that this reactivity order can serve selective arene functionalization. Rhodium-catalyzed 1,4-conjugate addition[34] to chalcone afforded **7c**,**d** in excellent yields. The palladium-catalyzed oxidative coupling of **6b** and **6d** with diaryl iodonium reagents[35] also proved efficient. Thus, bromide substituents on either coupling partner could be preserved to give **7e**,**f**, obviating problems with their activation in SMC (Scheme 3) and leaving scope for further derivatization. Acid **6f** underwent copper-catalyzed iodination with *N*-iodosuccinimide to give **7g** in 93% yield. This transformation is notable given the paucity of general methods reported for the iodination of electron-poor heteroaryl boronic acids. Copper-catalyzed Chan–Lam amination[36] (products **7h**,**i**) further highlights the unique versatility of the boryl (hetero)aryne building blocks: the same nucleophile may be introduced by using either the electrophilic (aryne) or nucleophilic (boronate) functionality under mild conditions with *meta* selectivity with respect to R (compare **4b**,**c** and **7h**,**i**).

To the best of our knowledge, the transformations in Schemes 1, 3, and 5 (reactions i, iii–vi) are the first to use *ortho*-silyl (hetero)aryl triflates as substrates in catalysis not involving activation of the aryne or mediation of its reactivity by a transition metal.[11,37] This points to broad new possibil-

ities for incorporating aryne precursors into more complex chemical environments.

In summary, we have developed a class of arylation reagents able to deliver orthogonally boronate or aryne reactivity for a wide variety of transformations. They enable the postfunctionalization of *ortho*-silyl (hetero)aryl triflate aryne precursors and significantly expand the options available for decorating aryl boronates selectively. The generality inherent in this approach offers a flexible new route to diversely functionalized (hetero)aromatic compounds.

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Keywords: arynes · boron · C–H activation · chemoselectivity · synthetic methods

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